

# Influence of PTFE coating on gas diffusion backing for unitized regenerative polymer electrolyte fuel cells

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## Abstract

Gas diffusion backings (GDBs) with various PTFE loadings for unitized regenerative polymer fuel cells (URFCs) were prepared and the relations between the PTFE loading amount and the URFC performance were examined. As for the GDB of the hydrogen electrode, both the fuel cell and water electrolysis performances were not affected by the amount of PTFE loading on the hydrogen side GDB. However, the URFC performances significantly depended on the PTFE loading amount of the GDB for the oxygen electrode; during the fuel cell and water electrolysis operations, URFC showed higher performances with smaller PTFE loadings but the cell with no PTFE-coated GDB showed a very deteriorated fuel cell performance. Cycle properties of the URFC revealed that the efficiency of the URFC decreased with the increasing cycles when the PTFE loading on oxygen side GDB was too low, however, a stable operation can be achieved with the appropriate PTFE loading on the GDB.

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## 1. Introduction

In terms of global energy and environmental problems, the replacement of fossil fuels by regenerative energy is being considered all over the world [1]. The utilization of hydrogen as an energy medium is believed to be an ideal energy system because of its high conversion efficiency, regenerative and zero-emission properties. A unitized regenerative fuel cell (URFC) is an electrochemical cell working both as a fuel cell and water electrolyzer, so that URFC is an energy storage device using hydrogen as the energy medium [2–6]. Accordingly, URFC could be likely to play an important role in meeting the desire for the utilization of hydrogen. Regenerative fuel cell systems have the advantages of long-term energy storage because of they are free from self-discharge, and theoretically higher energy densities compared to secondary batteries such as Ni/MH or Li-ion [7]. However, the round-trip energy conversion efficiency (electric power → hydrogen storage → electric power) of the URFC is still

lower than that of batteries. Therefore, an improvement in efficiency is necessary for the practical use of URFC.

To improve the efficiency of URFC, both the highly active bifunctional catalyst for O<sub>2</sub> redox reactions and the water management in the electrodes are quite important because most of the polarization in the URFC is on the O<sub>2</sub> electrode side. Although the development of active catalyst materials and the catalyst layer structures have been described in several reports [8–13], the water management in the gas diffusion backing (GDB) of the URFC has never been discussed. For polymer electrolyte fuel cells, highly hydrophobitized carbon paper or carbon cloth is usually adopted as the GDB materials, however, they cannot be used as the GDB of a URFC for the following two reasons: (1) the carbon materials tend to corrode at high potentials on the O<sub>2</sub> electrode side during the water electrolysis operation, (2) GDBs have to achieve an appropriate balance between the hydrophobic and hydrophilic properties for both the fuel cell and water electrolysis operations as shown in Fig. 1. The fuel cell operation requires that the O<sub>2</sub> GDB have a hydrophobic property to prevent water flooding, on the other hand, water electrolysis requires that the GDB have a hydrophilic property to supply water to the O<sub>2</sub> electrode. As a corrosion-resistive

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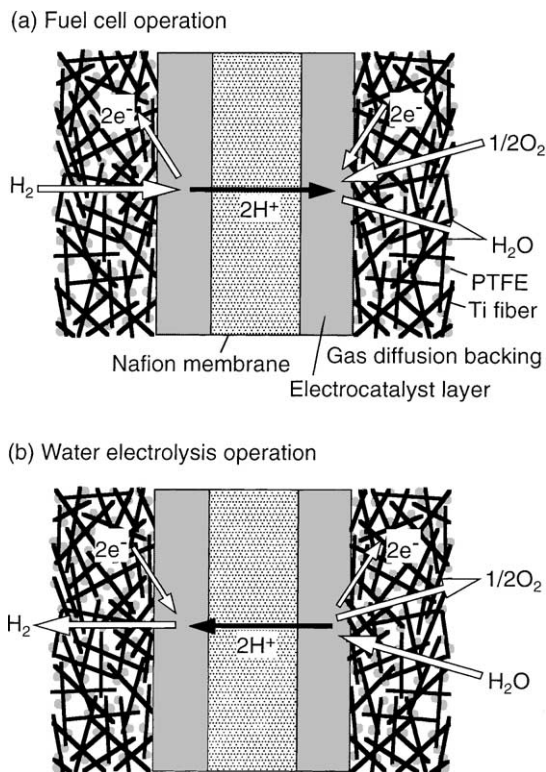


Fig. 1. Schematic illustrations of a unitized regenerative fuel cell (URFC) during (a) fuel cell operation, and (b) water electrolysis operation.

and electron conductive material in highly cathodic and acidic environments, titanium has been used as the current supplier material of a polymer electrolyte water electrolyzer using perfluorosulfonic acid membranes [14]. Therefore, titanium is a promising candidate for the GDB material of the URFC. In the present study, a variety of titanium GDBs coated with different amounts of PTFE were prepared and the URFC performance and durability were examined. Based on these results, the relation between the URFC performance and the hydrophobicity of the GDB was discussed.

## 2. Experimental

The electrocatalyst layers of the URFC were prepared in a similar manner as described in a previous report [12]. Commercially available fine platinum black powder (Johnson Matthey, specific surface area:  $26.1 \text{ m}^2 \text{ g}^{-1}$ ) was treated with a PTFE emulsion (Daikin, Polyflon) to increase the hydrophobic property of the catalyst, and the mixture was calcined at  $360^\circ\text{C}$  for 1 h to remove any organic additives. For preparing the oxygen electrode, the obtained Pt/PTFE (5 wt.% PTFE) was mixed with fine iridium black powder (Johnson Matthey, specific surface area:  $>20 \text{ m}^2 \text{ g}^{-1}$ ) at an atomic ratio of Pt/Ir = 85/15 because the catalyst mixture containing about 10–15 at.% shows a maximum URFC efficiency as previously reported [10]. The obtained powder was then thoroughly dispersed in 5 wt.% Nafion solution (Aldrich, 5 wt.% solution). The obtained catalyst slurry was

made into a thin layer by a doctor blade technique. The hydrogen electrode was also prepared by a similar procedure with the oxygen electrode except that the iridium black was not used. The catalyst loadings were about  $3\text{--}4 \text{ mg cm}^{-2}$  of Pt (and Ir). The catalyst layers were hot-pressed on the pre-treated Nafion 115 membrane [15] at  $150^\circ\text{C}$  to form the membrane electrode assembly (MEA).

A sintered titanium fiber substrate (0.5 mm thick, 75% porosity) was used as the GDB of the URFC. After the Ti fiber substrates were dipped in appropriate PTFE emulsions and dried at  $110^\circ\text{C}$  in air, the substrate was heated at  $360^\circ\text{C}$  for 1 h in a flowing  $\text{N}_2$  atmosphere to remove any organic and volatile additives contained in the emulsion. The treated substrate was cut into the same shape as the electrode, and the obtained GDBs were hot-pressed on both sides of the MEA at  $90\text{--}150^\circ\text{C}$ .

The test cell and the procedure for the URFC performance evaluation were described in previous papers [11,12]. Briefly, the terminal voltage vs. current density ( $I\text{--}V$ ) characteristics of the URFC were galvanostatically measured using a constant current supply and then the internal resistance of the cell was also determined by the current interruption method. During the fuel cell operation, the test cell was operated at  $80^\circ\text{C}$ , and fully humidified  $\text{H}_2$  and  $\text{O}_2$  at  $80^\circ\text{C}$  were supplied to the cell at a rate of  $100 \text{ ml min}^{-1}$ . The corresponding fuel and oxidant utilization were calculated to be 35 and 18% at  $500 \text{ mA cm}^{-2}$ , respectively. During the water electrolysis operation, ultra-purified water (Organo, Puric-MX) was supplied from the thermostated water reservoir to the bottom of both electrode sides of the test cell and the produced  $\text{H}_2$  and  $\text{O}_2$  gases and unreacted water evolved from the top of the cell. Water circulation spontaneously took place by the evolved gas-lifting on the  $\text{H}_2$  electrode side, however, water was supplied to the  $\text{O}_2$  electrode by forced circulation at a rate of  $75 \text{ ml min}^{-1}$ . The cell and the water reservoir were kept at  $80^\circ\text{C}$  and atmospheric pressure.

## 3. Results and discussion

Fig. 2 shows the apparent density of the coated PTFE on a Ti substrate as a function of the PTFE concentration in the emulsion. The amount of the coated PTFE was determined by measuring the weight of the substrates before and after the PTFE coating procedure. The coated PTFE amount was controlled almost linearly up to  $600 \text{ mg cm}^{-3}$  by adjusting the concentration in the emulsion between 0.6 and 60 wt.% PTFE. In order to examine the effect of the PTFE coating on the URFC performance, the  $I\text{--}V$  curves of a cell with different amounts of PTFE coatings on the Ti GDB were measured.

### 3.1. PTFE coating on GDB for $\text{H}_2$ electrode

To confirm the relation between the URFC performance and the PTFE coating on the GDB of the  $\text{H}_2$  electrode, the

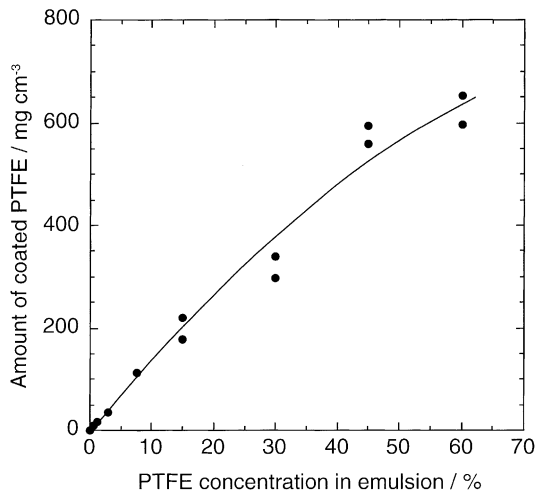


Fig. 2. Relation between the amount of coated PTFE on GDB and PTFE concentration in emulsion.

$I$ – $V$  curves of the cell with different amounts of PTFE coatings ( $16$  and  $559$   $\text{mg cm}^{-3}$ ) on the GDB of the  $\text{H}_2$  electrode side were measured as shown in Fig. 3. In these measurements, the amount of PTFE coating on the  $\text{O}_2$  electrode side was kept constant at  $16$ – $18$   $\text{mg cm}^{-3}$ . These  $I$ – $V$  curves of both the fuel cell and water electrolysis operation were nearly equivalent regardless of the coated PTFE amount on the GDB; this fact indicated that the URFC performance was almost independent of the PTFE coating amount on the  $\text{H}_2$  side within the investigated range. Thus, the amount of the coated PTFE on the  $\text{H}_2$  side was fixed at about  $560$   $\text{mg cm}^{-3}$  for the following measurements unless otherwise indicated.

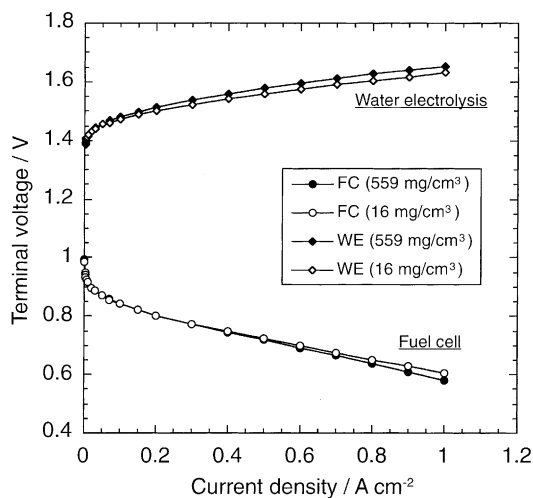


Fig. 3. Terminal voltages vs. current density curves of  $10\text{cm}^2$  URFCs with different PTFE loadings on the GDB of the hydrogen side. Fuel cell: the cell operated with  $\text{H}_2/\text{O}_2$  at  $80^\circ\text{C}$  and atmospheric pressure, respective flow rate of  $100/100\text{ml min}^{-1}$ , humidification temperature of  $80^\circ\text{C}$ . Water electrolysis: the cell operated with purified water at  $80^\circ\text{C}$  and atmospheric pressure.

### 3.2. PTFE coating on GDB for $\text{O}_2$ electrode

Similar measurements were also done for the GDBs on the  $\text{O}_2$  electrode side. Fig. 4 shows the  $I$ – $V$  curves of the cell during fuel cell operation with different amounts of PTFE coatings ( $0$ – $594$   $\text{mg cm}^{-3}$ ) on the GDB of the  $\text{O}_2$  electrode. Without a PTFE coating on the GDB, the fuel cell performance was very poor. This was probably due to water flooding in the GDB, because a similar behavior was observed when the electrocatalyst layer without PTFE was used as the  $\text{O}_2$  electrode [12]. With a small amount of PTFE ( $8.3$  or  $16$   $\text{mg cm}^{-3}$ ) coating on the GDB of the  $\text{O}_2$  electrode, the cell voltage dramatically recovered. This fact indicates that only a small amount of PTFE was sufficient to increase the hydrophobicity of the GDB and to prevent water flooding of the GDB and catalyst layer. However, further coatings of PTFE caused a performance degradation as shown in Fig. 4. The corresponding  $I$ – $V$  curves of the cell during the water electrolysis operation are shown in Fig. 5. Contrary to the fuel cell operation mode, the cell using the GDB without PTFE coatings showed superior performance (low terminal voltage), that is due to the smooth supply of water to the  $\text{O}_2$  electrode interface. PTFE loading on the  $\text{O}_2$  GDB caused an increase in the terminal voltage, that is due to the decrease in the water supply or the drying of the catalyst layer.

Based on the results of Figs. 4 and 5, the terminal voltage of the cell during the fuel cell and water electrolysis operations at  $500\text{mA cm}^{-2}$  was replotted as a function of the coated PTFE amount in Fig. 6. As expected from the  $I$ – $V$  curves, the voltage gradually decreased with the increasing PTFE loading during the fuel cell operation, whereas a steep increase in the cell voltage was observed with only a small amount of PTFE loading during water electrolysis. Too high PTFE coating caused an unstable fuel cell and reduced water

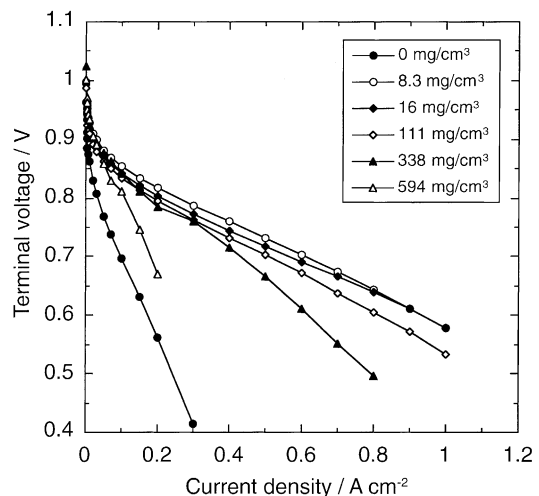


Fig. 4. Terminal voltages vs. current density curves of  $10\text{cm}^2$  URFCs during fuel cell operation with various PTFE loadings on the GDB of the oxygen side. The cell operated with  $\text{H}_2/\text{O}_2$  at  $80^\circ\text{C}$  and atmospheric pressure, respective flow rate of  $100/100\text{ml min}^{-1}$ , humidification temperature of  $80^\circ\text{C}$ .

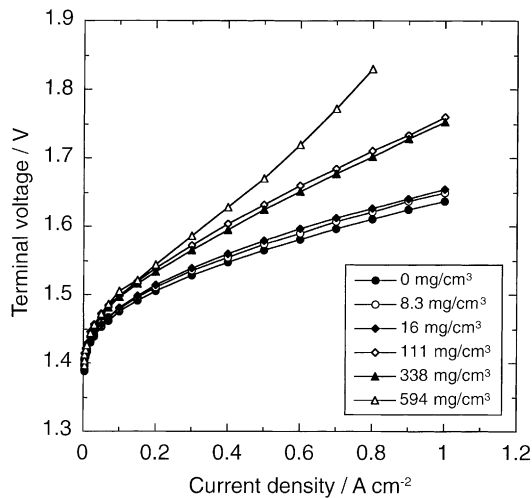


Fig. 5. Terminal voltages vs. current density curves of 10 cm<sup>2</sup> URFCs during water electrolysis operation with various PTFE loadings on the GDB of the oxygen side. The cell operated with purified water at 80 °C and atmospheric pressure.

electrolysis performance. On the basis of the voltages shown in Fig. 6, the energy conversion efficiency of the round-trip operation,  $\eta$  (electric power  $\rightarrow$  hydrogen  $\rightarrow$  electric power) can be calculated using the following equation [10]:

$$\eta = \frac{\text{terminal voltage (fuel cell)}}{\text{terminal voltage (water electrolysis)}} \quad (1)$$

and the calculated efficiencies at 500 mA cm<sup>-2</sup> are shown in Fig. 7 as a function of the coated PTFE amount. It was found that the maximum conversion efficiency of the URFC was obtained using a very small amount of PTFE loading.

Fig. 8 shows the  $I$ - $V$  curves of the cell using the O<sub>2</sub> GDB of 16 mg cm<sup>-3</sup> PTFE loading up to the 4th fuel cell/water electrolysis (FC/WE) cycle. No noticeable degradation was

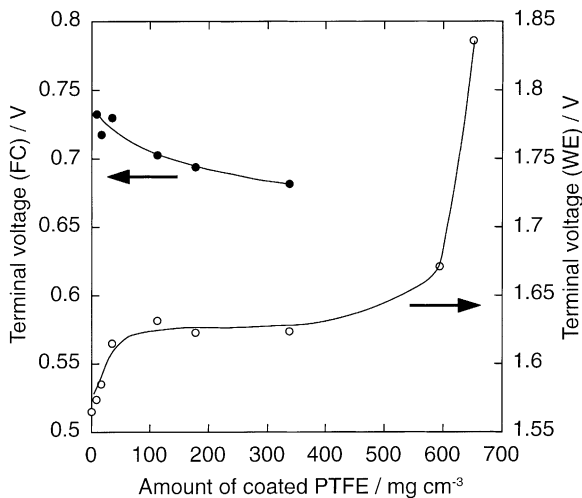


Fig. 6. Terminal voltages of the cell during fuel cell and water electrolysis operations at 500 mA cm<sup>-2</sup> as a function of the coated PTFE amount on the GDB of the oxygen electrode. URFC operating conditions: see Figs. 4 and 5.

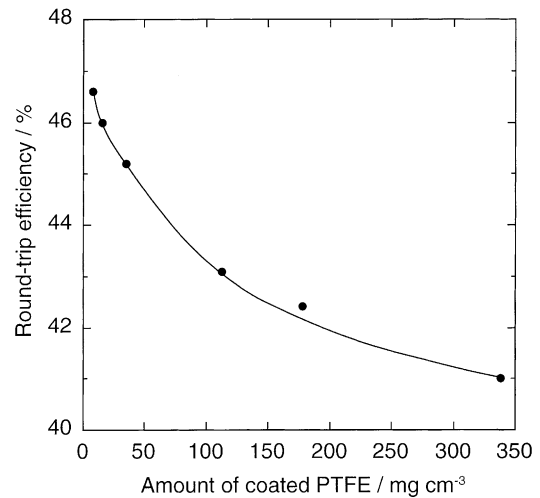


Fig. 7. Energy conversion efficiencies for round-trip operation of URFC at 500 mA cm<sup>-2</sup> as a function of the amount of the coated PTFE on the GDB of the oxygen electrode. URFC operating conditions: see Figs. 4 and 5.

observed for both the fuel cell and water electrolysis operations over the 4th cycle, whereas the  $I$ - $V$  curves during the fuel cell operation show some scatter. This is probably due to the difference in the water content in the electrocatalyst layer and the GDB. When the operation mode was switched from water electrolysis to fuel cell, the water in the cell was drained and the cell was purged with dry N<sub>2</sub> gas in order to remove any excess water contained in the electrode and GDB. Thus the fuel cell performance is affected to some extent by the previous water electrolysis and N<sub>2</sub> purging process. Fig. 9 shows the terminal voltage of the cell with different PTFE loadings on the O<sub>2</sub> GDB at 500 mA cm<sup>-2</sup> for each cycle. The cell using the O<sub>2</sub> GDB of 16 mg cm<sup>-3</sup> PTFE loading was operated without any performance loss during the fuel cell and water electrolysis cycles, however,

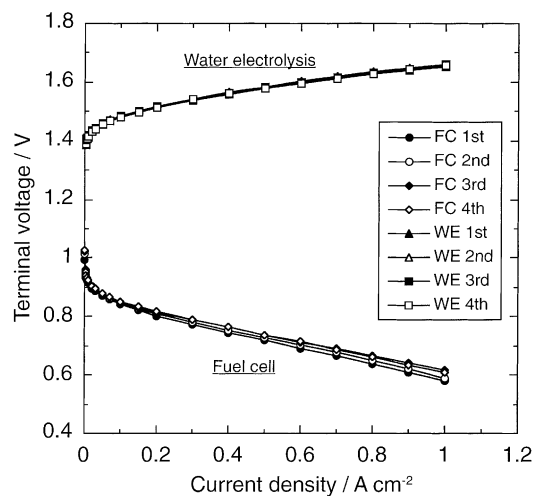


Fig. 8. Terminal voltages vs. current density curves of 10 cm<sup>2</sup> URFCs for the first to 4th fuel cell/water electrolysis cycles. GDB (oxygen side): 16 mg cm<sup>-3</sup> PTFE. Other URFC operating conditions: see Figs. 4 and 5.

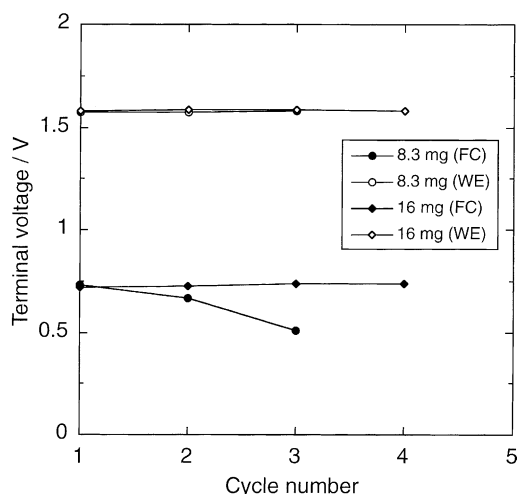


Fig. 9. Fuel cell/water electrolysis cycling of URFC operated at  $500 \text{ mA cm}^{-2}$ . URFC operating conditions: see Figs. 4 and 5.

the cell with the  $8 \text{ mg cm}^{-3}$  PTFE loading showed considerable voltage loss during the fuel cell operation with increasing FC/WE cycles. Considering that the water electrolysis was operated without degradation, this voltage loss should be due to the decline in the hydrophobicity of the GDB. It is likely that part of the coated PTFE is removed from the GDB during the FC/WE cycles when the PTFE coating amount was not sufficient. Accordingly, reducing the PTFE loading on the  $\text{O}_2$  GDB is beneficial from the point of view of the conversion efficiency as shown in Fig. 7, however, a PTFE loading greater than  $16 \text{ mg cm}^{-3}$  is necessary to sustain durability of the URFC cycle performance.

#### 4. Conclusions

The relations between the PTFE coating amount on the GDB and the URFC performance were examined. The PTFE coating on the GDB of the  $\text{H}_2$  electrode did not affect the cell performance, however, the URFC performance significantly depended on the coatings on the  $\text{O}_2$  electrode side. The cell with the smaller PTFE loading amount on the  $\text{O}_2$  GDB exhibited a higher fuel cell and lower water electroly-

sis voltage, i.e., higher round-trip efficiency. The results of the alternate operations between fuel cell and water electrolysis cycle tests revealed that a stable operation of the URFC cycle was achieved using the appropriate amount of PTFE loading on the GDB ( $16 \text{ mg cm}^{-3}$ ). Many more cycle tests are indispensable for evaluating practical durability, however, this work showed that the PTFE loading amount of the  $\text{O}_2$  side GDB is one of the keys for improving the URFC performance.

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